

## PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT  
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PPD 70193/WO	<b>FOR FURTHER ACTION</b>	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)
International application No. PCT/GB 03/05291	International filing date (day/month/year) 05.12.2003	Priority date (day/month/year) 06.12.2002
International Patent Classification (IPC) or both national classification and IPC A01N25/04, A01N25/10		
Applicant SYNGENTA LIMITED et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 6 sheets, including this cover sheet.
  - This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.
3. This report contains indications relating to the following items:
  - I  Basis of the opinion
  - II  Priority
  - III  Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
  - IV  Lack of unity of invention
  - V  Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
  - VI  Certain documents cited
  - VII  Certain defects in the international application
  - VIII  Certain observations on the international application

Date of submission of the demand 02.06.2004	Date of completion of this report 19.04.2005
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Muellner, W Telephone No. +31 70 340-3289



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB 03/05291

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, Pages**

1-39 as originally filed

**Claims, Numbers**

1-22 received on 12.01.2005 with letter of 10.01.2005

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

5.  This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

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**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes: Claims	1-22
	No: Claims	
Inventive step (IS)	Yes: Claims	1-22
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-22
	No: Claims	

**2. Citations and explanations**

**see separate sheet**

**Re Item V**

**Reasoned statement with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement**

Reference is made to the following documents

D1: US-B-6 262 1521  
D2: EP-A-0 007 731

The amendments filed with letter of 10.01. do not go beyond the disclosure in the international application as filed 70.2(c). The amended independent claim 1 corresponds to originally file dependent claim 21. Amended independent claim 22 corresponds to originally file independent claim 23 having the analogous further restriction.

**Novelty**

The present application meets the criteria of Article 33(1) PCT, because the subject-matter of claims 1-22 is new in the sense of Article 33(2) PCT.

Independent claim 1 relates to a method for stabilising particulate suspensions of agrochemicals in aqueous phase containing no water miscible organic solvent, which method comprises forming a polymeric stabiliser having hydrophobic and hydrophilic moieties and functional groups capable of undergoing cross linking reactions and reacting these groups with substances present in the composition and capable of cross linking. The ratio by weight of the polymeric stabiliser to the suspended agrochemical is from 1:200 to 1:10.

Independent claim 22 refers to suspension resulting from applying the method of claim 1. However, it is not restricted to agrochemicals as the suspended solids.

Document D1, which is already cited in the application as originally filed, discloses (cf. the passages cited in the international search report) the stabilisation of suspensions by in-situ cross linking polymeric stabilisers having hydrophobic and hydrophilic moieties and functional groups capable of undergoing cross linking reactions and reacting these groups with substances present in the composition and capable of cross linking. As field for applying such suspensions i.a. agriculture (e.g. insecticides) is mentioned. The vehicle may be water, organic solvents or combinations thereof, with a strong preference to utilize

aqueous based dispersions.

No mentioning is made of the ratio by weight of the polymeric stabiliser to the suspended solid. All examples relate to aqueous pigment dispersions having a ratio by weight of polymer to suspended pigment of 2:3.

Consequently the subject-matter of claims 1-22 is considered to be novel over-the disclosure of D1, since the specific feature of a ratio by weight of the polymeric stabiliser to the suspended agrochemical of in the above range is not disclosed in D1.

Document D2 discloses (cf the passages cited in the international search report) the stabilisation of suspensions of hydrophobic pesticide particles with co-polymers comprising hydrophobic and hydrophilic groups. It is not suggested to further crosslink such co-polymers with the aid of suitable additional groups and agents. Consequently the subject-matter of claims 1-22 is also novel with regard to the disclosure of D2.

#### **Inventive Step**

The present application meets the criteria of Article 33(1) PCT, because the subject-matter of claims 1-22 involves an inventive step in the sense of Article 33(3) PCT.

The problem underlying the present application can be seen as the provision of a method for stabilising aqueous suspension of water insoluble agrochemicals and corresponding stabilised suspensions.

The solution according to claim is characterised by the use of certain co-polymers within a certain range of relative amounts and their cross linking in situ.

The closest prior art is represented by document D1, which exemplifies the basic principle by preparing pigment dispersions for inks suitable for use in inkjet printing devices. D1 describes the particles as being entangled in the cross-linked polymer matrix.

No mentioning is made of the ratio by weight of the polymeric stabiliser to the suspended solid. However, all examples relate to aqueous pigment dispersions having a much higher ratio by weight of polymer to suspended pigment of 2:3.

It is not suggested nor seems it obvious in the light of the concept of 'entanglement' that the ratio could be lowered considerably below the exemplified ratio to the ratio which in D2 is used with non-crosslinked surface active co-polymers.

Further, although D1 states that aqueous based vehicles are strongly preferred wherever possible, it appears that addition of substantial amounts of water-miscible solvent, e.g.

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isopropanol, is actually required. This would have negative effects on the stability of suspensions of many agrochemicals, since they are often, in contrast to ink-jet pigments quite soluble in such solvents resulting in crystal growth due to Ostwald ripening. This would also discourage the skilled person to apply the method of D1 for agrochemicals.

Starting from D2 the subject-matter of independent claims 1 and 22 seems not obvious either. D2 suggest that the advantage of co-polymers comprising hydrophobic and hydrophilic groups over conventional dispersing agents is due to the strength of attachment to the surface of the hydrophobic particles (cf. D2, page 9, lines 11-18). In the light of the teaching of D1 one could consider to permanently 'entangle' the agrochemicals in an attached block or graft polymer by additionally introducing crosslinkable groups and reacting with cross linking agents in situ. However, the skilled person would then also apply the conditions specified in D1, i.e. use a higher ratio and an auxiliary water-miscible solvent.

**Industrial Applicability**

The subject-matter of claims 1-22 is considered to be industrially applicable (Article 33(1) and (4) PCT).

CLAIMS

1. A method of enhancing the stability of a particulate suspension comprising an aqueous phase containing substantially no miscible organic solvent having suspended therein an agrochemical solid substantially insoluble in said aqueous phase which comprises

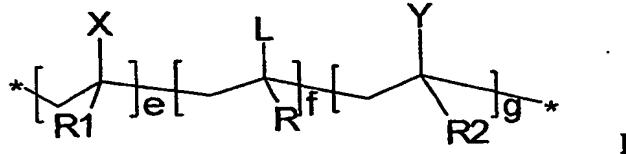
5 (i) forming a polymeric stabiliser having a hydrophilic moiety and a hydrophobic moiety by polymerising a plurality of vinylic monomers, not being exclusively vinylic esters or their hydrolysed products, at least some of which contain functional groups capable of undergoing cross-linking reactions and

10 (ii) reacting said polymeric stabiliser with one or more substances contained (dissolved or suspended) in the aqueous phase capable of undergoing a cross-linking reaction with said functional groups; wherein the ratio by weight of (a) the polymeric stabiliser prior to cross-linking to (b) the suspended agrochemical is from 1 part of polymeric stabiliser to 200 parts of suspended agrochemical to 1 part of polymeric stabiliser per 10 parts of suspended agrochemical.

15 2. A method according to claim 1 wherein the solid is milled or otherwise dispersed in the presence of the aqueous phase and the polymeric stabiliser prior to step (ii).

3. A method according to claim 1 or claim 2 wherein the particle size of the suspended agrochemical is from 1 to 10 microns.

20 4. A method according to claim 1 wherein polymeric stabiliser is represented by the general formula (I):



25 wherein one \* represents the residue of an initiator group and the other \* represents the residue of a terminator group; R1, R and R2 are independently H or methyl; X is a hydrophilic moiety; L is a moiety containing a cross-linking group; Y is a hydrophobic moiety; the value of e is from 0 to 0.8; the value of f is from 0.05 to 0.4 and the value of g is from 0.10 to 0.90 and e + f + g equals 1, provided that when e is 0, \* represents the residue of a hydrophilic initiator.

5. A method according to claim 4 wherein the value of e is from 0.005 to 0.35, the value of f is from 0.01 to 0.4.

3,3'dimethyl-4,4'-biphenylene diisocyanate 4,4'-methylenebis(2-methylphenyl isocyanate); 3,3'dimethoxy-4,4'biphenylene diisocyanate; 2,4-tolylene diisocyanate; 2,6-tolylenediisocyanate; tetramethyl-4,4'-biphenylene diisocyanate; isophorone diisocyanate; hexane-1,6-diisocyanate; tetramethylene xylene diisocyanate;  $\alpha$ ,4-tolylene diisocyanate; tolylene 2,5-diisocyanate; 2,4,6-trimethyl-1,3-phenylene diisocyanate; poly(ethylene adipate) tolylene 2,4-diisocyanate terminated; poly(isophorone diisocyanate); poly(propylene glycol) tolylene 2,4-diisocyanate terminated; poly(1,4-butanediol) tolylene diisocyanate terminated; 1,8-diisocyanatooctane; poly(hexamethylene diisocyanate); poly(tolylene 2,4-diisocyanate); poly(tetrafluoroethylene oxide-co-difluoromethylene oxide)  $\alpha,\omega$ -diisocyanate; 1,4-diisocyanatobutane; 1,3-phenylene diisocyanate; 1,4-phenylene diisocyanate; trans-1,4-cyclohexylene diisocyanate; m-xylylene diisocyanate;  $\alpha,\alpha$ -dimethyl- $\alpha$ ,4-phenylethyl diisocyanate; 4-bromo-6-methyl-1,3-phenylene diisocyanate; 4-chloro-6-methyl-1,3-phenylene diisocyanate; poly(1,4-butanediol) isophorone diisocyanate terminated; 3,3'-dimethyl-4,4'-biphenylene diisocyanate; and 1,3-bis(1-isocyanato-1-methylethyl)benzene.

20 A method according to any of claims 2 to 19 wherein the substance dissolved or suspended in the aqueous phase and capable of undergoing a cross-linking reaction is added to the aqueous phase after milling.

20 21 A method according to any of the preceding claims wherein the polymeric stabiliser is prepared by atom transfer radical polymerisation.

22 A particulate suspension comprising a liquid phase having suspended therein a solid substantially insoluble in said liquid phase wherein the suspension is stabilised by the reaction product of

25 (i) a polymeric stabiliser having a hydrophilic moiety and a hydrophobic moiety and comprising a plurality of vinylic monomers, not being exclusively of vinylic esters or of their hydrolysed products, at least some of which contain functional groups capable of undergoing cross-linking nucleophilic or condensation reactions and

—

30 (ii) one or more substances contained in the liquid phase capable of undergoing a cross-linking reaction with said functional groups;

wherein the ratio by weight of (a) the polymeric stabiliser prior to cross-linking to (b) the suspended solid is from 1 part of polymeric stabiliser to 200 parts of suspended solid to 1 part of polymeric stabiliser per 10 parts of suspended solid.

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